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PROCESS FOR PRODUCING CONJUGATED DIENE POLYMERS

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3 Claims

ABSTRACT OF THE DISCLOSURE

Conjugated diene polymers are produced by reacting from 0.5 to 2 moles of a haloalkyleneoxide with one mole of a living polymer prepared by reacting a conjugated diolefin or a mixture of the conjugated diene with a vinyl compound having the formula: $\text{CH}_2=\text{CR}_1\text{R}_2$, wherein R_1 represents a hydrogen atom or an alkyl group and R_2 represents an aryl group or a pyridyl group in the presence of an alkali metal or an organoalkali metal compound.

BACKGROUND OF THE INVENTION

Field of the Invention

This invention relates to a process for producing a reactive liquid conjugated diene polymer.

Description of the Prior Art

Various processes for producing conjugated diene polymers containing reactive groups such as epoxy, hydroxyl, etc., are well known to those skilled in the art. For instance, processes such as the reaction between a large excess of epichlorohydrin and a living polymer such as polybutadiene, and the reaction of a polyepoxide such as limonene diepoxide with living polybutadiene are well known. However, deficiencies are inherent in the products of both reactions. The polymers prepared by the former process have reactive groups only as the terminals of the polymer, which result in a polymer difficult to cure. The polymers prepared by the latter process can be cured, but the cured polymers are much too brittle. Therefore, these products have not been of much commercial value.

SUMMARY OF THE INVENTION

Accordingly, it is an object of this invention to provide a process for producing a conjugated diene polymer containing pendant reactive moieties such as an hydroxyl group, a carboxyl group or a polymerizable unsaturated bond in the polymer chain.

It is another object of this invention to provide a process for producing a liquid conjugated diene polymer which is easily processed.

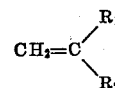
Yet another object of this invention is to provide a process for producing a liquid conjugated diene polymer which is easily cured to form various products from rubber-like elastomers to hard resins by treating the reactive group in the chain with a compatible curing agent.

Still another object of this invention is to provide a process for preparing a conjugated diene polymer useful in various applications such as electric insulators, sealers, shock absorbers, etc.

These and other objects of this invention can be attained by reacting from 0.5 mole to 2 moles of a haloalkylene oxide with one mole of a living polymer which is prepared by reacting an alkali metal or an organoalkali metal compound with a conjugated diene or a mixture of

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a conjugated diene and a vinyl compound having the formula:



wherein R_1 represents a hydrogen atom or an alkyl group, and R_2 represents an aryl group or a pyridyl group.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The living polymers used as the starting material in this invention are liquid polymers having an alkali metal at both ends of the polymer. The polymers are prepared by reacting an alkali metal or an organo-alkali metal compound with a conjugated diolefin or a mixture of a conjugated diolefin and a vinyl compound and range in molecular weight from 500 to 10,000, and especially from 1,000 to 5,000. In order to prepare cured polymeric products having excellent low temperature characteristics, it is preferable to have a greater content of conjugated diolefin or diene units in the living conjugated diene polymer than vinyl units, and especially preferable to have 30% more diene units than vinyl units. The conjugated dienes, which are used as the monomer starting material of the liquid living polymer, can be butadiene-1,3; 2-methylbutadiene-1,3; pentadiene-1,3; 2,3-dimethylbutadiene-1,3; 1-phenylbutadiene-1,3, etc.

Vinyl compounds having the formula: $\text{CH}_2=\text{CHR}_2$ used in conjunction with a conjugated diene can be vinyl aromatic compounds such as styrene, α -methylstyrene, tert-butylstyrene, paramethoxystyrene and vinyltoluene; and vinyl pyridines such as 2-vinylpyridine and 4-vinylpyridine. The amount of the vinyl compound employed is dependent upon the physical characteristics desired in the cured product polymers and is usually less than 75 weight percent, preferably less than 50 weight percent and especially less than 25 weight percent based on the total monomer content of the product polymers.

The alkali metal used as the initiator in the process can be lithium, sodium, potassium, rubidium, cesium, etc. The organoalkali metal compound used as the initiator can be an alkali metal complex of naphthalene, anthracene and biphenyl; a complex of dienes, such as the dimer, trimer and tetramer lithium complex of butadiene and isoprene; a complex of styrene and a dialkali metal hydrocarbon compound such as 1,4-dialkali metal butane, 1,5-dialkali metal pentane, 1,10-dialkali metal decane, 1,2-dialkali metal-1,2-diphenylethane, 1,4-dialkali metal-1,4-tetraphenylbutane. When a liquid living conjugated diene polymer having a high content of diene units is desired, lithium metal or organolithium compounds such as the dimeric lithium complexes of butadiene or isoprene are preferably used.

The alkali metal complexes of conjugated dienes can be prepared by the following process. An alkali metal is reacted with a polycyclic aromatic compound at -20 – 30°C ., preferably 0 – 25°C ., in a diluent to form an alkali metal complex of the polycyclic aromatic compound. The polycyclic aromatic compound can be naphthalene, biphenyl, phenanthrene, anthracene, etc., and is usually employed in the diluent at concentrations ranging from 200 to 500 millimole per litre. The polycyclic aromatic compound-alkali metal adduct is filtered to remove unreacted alkali metal, and then is reacted with any one of said conjugated dienes. It is necessary to conduct the reaction at temperatures lower than 0°C . to prevent the formation of higher polymerization products of the conjugated diene. Preferably, the reaction is conducted at temperatures lower than -20°C . and as low as -78°C . Suitable diluents include aprotic Lewis bases such as aliphatic